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Supercritical Carbon Dioxide Extraction of Spent Bleaching Clays†**

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The disposal of spent bleaching clay generated in the vegetable oil processing industry is a potential problem of environmental concern, due to the pyrophoric nature of the residual oil/clay mixture in landfills. This study describes the use of SC-CO_2 for processing both neutral and acidic clays used in the refining of soybean oil. Rapid extractions of spent bleaching clay can be affected at 10,000–12,000 psig by proper preparation of the clay substrate. Experiments utilizing both laboratory and pilot-plant extractors have yielded almost 100% of the adsorbed oil. Extraction of the clay can be facilitated by crossblending the clay with a diatomaceous earth-based dispersant. The oils recovered by the supercritical fluid extraction (SFE) process have properties (free fatty acid content, Lovibond color ratio, and phosphorus content) similar to those found for degummed-bleached oils.

Keywords: bleaching clay, carbon dioxide, oil refining, soybean oil, supercritical fluid.

INTRODUCTION

An average soybean oil refinery generates about 5,000 lbs of spent bleaching clay per day in the removal of odoriferous components and color bodies from refined feedstock. This processing aid must be treated to remove the adsorbed residual oil or be buried in a landfill after the bleaching step.[1] Several processes have been developed to strip residual oil from the clay matrix based on treatment of the clay with dilute caustic solution[2] or extraction of the oil using organic solvents.[3] These processes also produce unacceptable chemical residues which can impact negatively on the environment.[4]

Currently, spent bleaching clays from the vegetable oil processing industry are disposed of in landfills,[5] necessitating additional costs for transport of the clay from the refinery and its subsequent treatment at the fill site. At the landfill, the clay is frequently buried or treated with water, to reduce the probability of spontaneous combustion of the clay/oil mixture. With the exception of the recent study by Taylor and Jenkins,[6] little is known about the factors governing the pyrophoricity of spent bleaching clays.

Treatment of spent bleaching clays with supercritical carbon dioxide (SC-CO_2) presents an alternative to the above disposal methods. SFE utilizing carbon dioxide provides an environmentally acceptable solution for post refinery treatment of the clay, since CO_2 is nonflammable, nontoxic, and is a selective solvent for oleophilic materials. One study has been reported[7] in which supercritical propane and fluorocarbons were utilized in the treatment of spent clays imbibed with silicone and vegetable oils. Unfortunately, in this work, only one experiment was performed on a clay/vegetable oil mixture, resulting in a low recovery of the oil. For this reason, and to avoid the use of potentially explosive and environmentally unacceptable supercritical fluids, we initiated an extraction study using SC-CO_2.

EXPERIMENTAL PROCEDURES

Successful extraction of spent bleaching clays with SC-CO_2 can be achieved only by optimizing the experimental conditions. Rapid extraction of the oil from the clay was facilitated by conducting the extractions at 12,000 psig and 80 °C, a condition where the oil solubility in SC-CO_2 is maximized.[8,9] Such conditions have been shown by Cygnarowicz-Provost[10] to yield soybean oil at a slightly lower cost than oil obtained from the conventional liquid-extraction process.[10] The particle size of bleaching clays can also inhibit complete extraction of

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TABLE I
Typical Conditions for Lab and Pilot Plant Extractions

Parameter	Laboratory	Pilot Plant
extraction eessel	tubular (2' × 5/8" I.D.)	4-L vessel (3' × 3" I.D.)
extraction P & T	11,000 psig, 80 °C	12,000 psig, 80 °C
collection P & T	ambient	2,300 psig, 80 °C
CO_2 used	1.5–4.1 lbs	6–8 lbs
clay weight	0.09–0.25 lbs	5.1–8.5 lbs

the oil from the matrix, due to channeling of extraction fluid through the sorbent bed,[7] as well a compaction of the clay bed under high pressure. For this reason, studies were conducted both on laboratory and pilot plant scale. The pilot plant study utilized a captive CO_2 supply and as operated in a recycle mode, thereby permitting simulation of an industrial scale process.

Typical conditions utilized in the clay extraction studies are tabulated in Table I. The laboratory-scale extraction unit has been previously described.[9] Bleaching clay was poured into the specified tubular extraction vessel and extraction commenced at 11,000 psig and 80 °C. Extractions were continued until oil could no longer be removed from the receiver attached to the extraction system.

Pilot plant extractions were performed on the NCAUR (National Center for Agricultural Utilization Research) semi-continuous supercritical-fluid extraction unit shown in Figure 1. Details on the construction of the extractor, which has provision for recycling the extraction fluid, can be found in the literature.[11] Clay extractions were performed in one of the 4-L extraction vessels (A) shown in the schematic diagram. Extractions were conducted in this vessel at 12,000 psig and 80 °C using a CO_2 flow rate of approximately 0.5 lbs/min. The dissolved soybean oil in the SC-CO_2 was transported to the receiver vessel (R), which was operated at 2,300 psig and 40 °C. Under these conditions, soybean oil exhibits less than 0.1 wt % solubility in the compressed CO_2 and readily precipitates from the fluid phase. Extractions could be completed under the above conditions on 5.0–8.5 lbs charges of clay using 6–8 lbs of CO_2 that was then recycled over the clay. A total of 40–60 lbs of CO_2/run were recycled over the clay bed as measured by the mass flow meter.

The spent bleaching clays utilized in these studies were obtained from refineries operated by Riceland Foods (Stuttgart, AK) and Central Soya (Ft. Wayne, IN). Both neutral and acidic clays were incorporated in this study to test the effectiveness of SC-CO_2 extraction with respect to

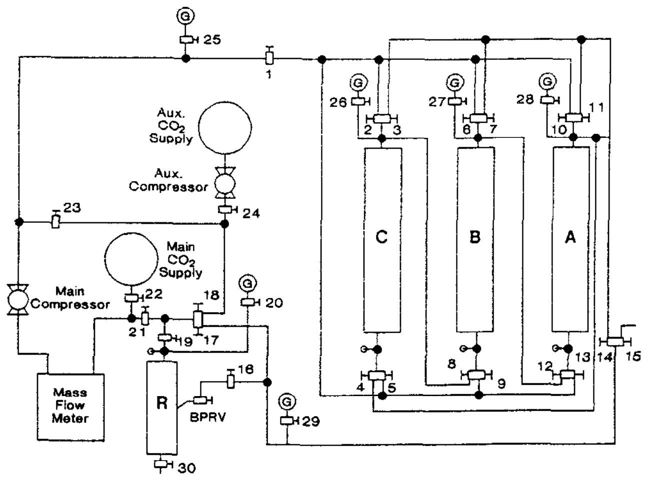

Figure 1. Semi-continuous supercritical-fluid extraction system.

TABLE II
SFE Experiments on Spent Bleaching Clays

Run	Clay Type	Extractor	% Oil Extracted*	Clay Prep
1	Neutral	Pilot	15.2%	
2	Neutral	Pilot	19.3%	
3	Neutral	Pilot	26.8%	Mixed
4	Neutral	Pilot	25.5%	Mixed
5	Neutral	Lab	32.1%	
6	Neutral	Lab	30.7%	Hydromatrix
7	Neutral	Pilot	30.9%	Hydromatrix
8	Acid	Lab	34.1%	
9	Acid	Pilot	32.6%	
10	Neutral	Pilot	26.5%	

*Total wt % of oil in clay ca. 32–34%

the clay structure. A pelletized diatomaceous earth, designated Hydromatrix, from Analytichem International (Harbor City, CA) was used in several experiments as an aid in dispersing the spent bleaching clay.

Samples of both the extracted clay and recovered oil were saved from each experiment. Selected oil samples were characterized with respect to their free fatty acid content (FFA), peroxide value (PV), Lovibond color ratios, and phosphorus content. Standard AOCS Methods[12] were used in performing these tests unless otherwise noted. The Lovibond color ratios of the extracted oils were determined using a computerized Colourscan system while the phosphorus content of the oils were analyzed by atomic absorption spectroscopy. Oil content of the clay was assessed by Soxhlet extraction with *n*-hexane.

RESULTS AND DISCUSSION

Experimental extraction results performed on both neutral and acidic bleaching clays are summarized in Table II. Initial experiments were conducted on the neutral bleaching clay matrix using the pilot-plant extractor. Extractions were terminated when oil could no longer be collected in the receiver vessel of the pilot plant. The oil recovered in Run 1, which is expressed as a weight percent of the total clay charge, was 15.2%. The extracted clay in this experiment was removed from the extraction vessel and analyzed for oil content. The residual oil level was found to be 8.8 wt % based on the initial clay charge. The results from this run indicated that either the extract on conditions or clay preparation were inadequate to effect total removal of the oil from the clay matrix.

An identical extraction (Run 2) was then performed to verify the results obtained in the first experiment. The oil yield in this case was found to be 19.3 wt %. Oil analysis on the extracted clay yielded a 7.2 wt % residual oil content, verifying that the extraction was not completed. These two initial results suggested that perhaps the oil distribution in the spent bleaching clay was not homogeneous and that mixing the substrate prior to extraction would enhance the efficiency of the extraction.

Two extractions (Runs 3 & 4) were then performed on the pilot-plant extractor to verify the above hypothesis. Oil yields for these two experiments were 26.8 and 25.5 wt %, respectively. Analysis of the SC-CO_2 extracted clays for residual oil content showed that considerable oil was still present in the extracted clays (Run 3 — 6.12 wt %, Run 4 — 8.8 wt %). A discrepancy was also apparent in the total oil mass balance, since combining the extracted and residual oil wt % for Runs 1, 2, 3, and 4 yielded 24.0, 26.5, 32.9, and 34.3 wt %, respectively. It was obvious that remixing the spent bleaching clay did not assure total extraction of all available oil.

Determination of the total oil content in the spent clay matrix via Soxhlet extraction is at best difficult due to the fine particle size of clay and its tendency to agglomerate in the Soxhlet extraction device. Accurate analytical determination of the total oil content of the neat spent bleaching clay is essential in order to assess the extraction efficiency of the SFE process. Several exhaustive extractions of the starting clay material were made with the aid of a dispersing agent to establish the residual oil content of the sorbent. In this procedure, the spent bleaching clay was mixed in a weight ratio of 2:1 with pelletized diatomaceous earth (Hydromatrix) to disperse the clay sample. This modification of the Soxhlet procedure facilitated contact between the clay matrix and extraction solvent and yielded consistent analytical results. The Soxhlet extraction values on the samples used in Runs 2, 3, and 4 were determined to be 31.7, 31.1, and 32.8 wt %. The accuracy of these figures was further verified by running an extraction of spent bleaching clay in the small laboratory tubular extractor (Run 5) which yielded 32.1 wt % of oil based on the initial clay charge. Soxhlet extraction of this clay sample gave 32.0 wt % oil, a value in excellent agreement with the result obtained from SC-CO_2 extraction and the previously quoted Soxhlet-derived data. These results suggest that SC-CO_2 extraction could be used as an alternative to Soxhlet extraction with liquid hydrocarbon solvents.

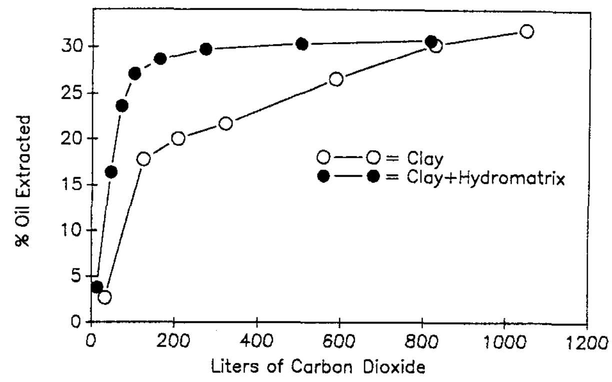

Figure 2. Comparison of oil extraction rates for clay vs. clay + hydromatrix.

The consistent results obtained by using the Hydromatrix dispersant in the modified-Soxhlet procedure suggested that the use of a dispersion agent in the SFE of clays would enhance the recovery of the soybean oil. Consequently an experiment was run using the laboratory scale extractor loaded with 40 g of the spent clay plus 20 g of Hydromatrix. The total yield of oil from this experiment (Run 6) was 30.7%. In addition, it was noted that the inclusion of Hydromatrix decreased the time of the extraction by 1/3 and required less than half the extraction fluid needed for the SFE of the neat clay. This improvement in the kinetics of extraction is shown in Figure 2. Compaction of the spent bleaching clay bed in the extractor, with the attendant large pressure drop, is also avoided by using the dispersant for the SFE. It should be noted that the SFE extracted clay can be readily separated from the Hydromatrix by a No. 45 mesh screen, thereby facilitating reuse of the dispersant in an actual industrial operation.

A similar experiment to the previous one was performed in the 4-L pilot plant vessel using a 2:1, clay to Hydromatrix charge. In this case, a 30.7 wt % oil yield was obtained after recycling the CO_2 through the extractor bed. This result is in excellent agreement with the value obtained on the small laboratory extractor and exceeds the yields recorded on neat clay beds (Runs 1–4). This result was further verified by running another SFE on the neat clay in a 4-L extraction vessel (Run 10). The yield of only 26.5 wt % oil, clearly confirms the enhancement of oil yield by incorporation of the dispersant into the SFE scheme. Additional pilot plant runs were performed on an acidic spent bleaching clay from another industrial source. Extraction of this clay in the laboratory unit (Run 8) gave a 34.1 wt % yield. This result compared favorable with the Soxhlet-measured oil content of 34.6 wt %. A pilot plant run was also made on the acidic clay, and produced a oil yield of 32.6 wt % (Run 9). It therefore appears, that the SC-CO_2 extraction of spent bleaching clays is equally applicable to both neutral and acidic matrices.

TABLE III
Properties of Oils Extracted from Spent Bleaching Clays

Run	FFA (%)	PV (meg/Kg)	Lovibond Color	Phosphorus (ppm)
1	0.45	1.9	44.0Y/2.7R	0
2	0.48	1.5	43.0Y/2.7R	0.16
3	0.48	1.2	44.0Y/2.7R	0.46
4	0.49	1.1	50.0Y/3.1R	0.16
7	0.87	2.9	69.0Y/12.1R	0.51
9	0.39	3.5	68.0Y/5.3R	0.30
10	0.57	7.7	70.2Y/13.4R	2.00

Several physical and chemical tests were run on selected oil samples taken from various experimental runs. The results of these tests, which included measurement of the oil's free fatty acid content, peroxide value, Lovibond color ratio, and phosphorus content, are listed in Table III. Overall, the results in Table III indicate that the oils recovered from the SFE of spent bleaching clays, are approximately equivalent to a conventional degummed-bleached oil.[13] Hence, these oils would be suitable for a number of industrial applications that do not require food grade oil specifications. Further refining of the SFE-derived oils would be needed in order to lower their free fatty acid content and peroxide value. It should be noted that the elevated peroxide levels may be due to the extended time lapse (approximately one month) which occurred between collection of the clay sample at the soybean oil processing plant and the SFE-processing of the clays at NCAUR.

A visual examination of the SFE-extracted bleaching clays revealed that a reduction in color had been achieved when they were compared to the original product from the oil refinery. However, the SFE-treated clay still contained more pigment matter than the virgin clay. The bleaching power of treated and recycled clays has been studied by Ong and Sinkeldam,[12] who found that the bleaching power was 50% less than that achieved by using fresh clay. For this reason, no further studies were attempted to assess the bleaching power of the SC-CO_2 treated clays.

In conclusion, the above SFE results show that quantitative recovery of soybean oil from neutral and acidic spent bleaching clays is possible using CO_2. Experiments conducted in both laboratory and pilot plant extractors yielded variable oil recovery results, unless suitable precautions were taken to avoid fluid channeling and bed plugging. The use of a dispersing agent was found to enhance contact between the oil and the SC-CO_2 and to lead to an improvement in the extraction kinetics. An improved method was developed for analytically determining residual oil levels by Soxhlet extraction. Finally, we have shown spent clays can be treated readily in semi-continuous extraction mode, yielding an industrial-grade soybean oil and oil-free clay.

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